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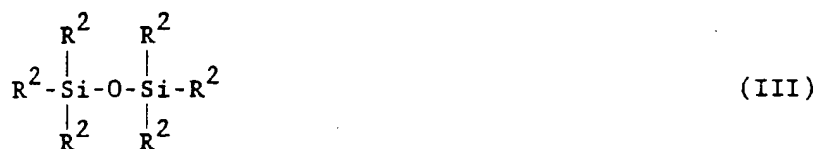
(54) **Thioglycolamide-functional siloxanes.**

(57) Disclosed are thioglycolamide functional siloxanes and their salts which are prepared from the reaction between an amine-functional siloxane and thioglycolic acid or a thioglycolic ester. These materials are useful as reducing agent in the perming process. They are also useful in conditioning the hair.

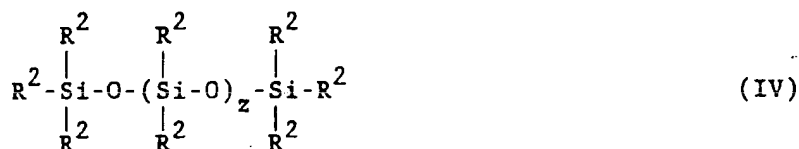
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The linear amine functional siloxanes useful in this invention are selected from the groups comprising



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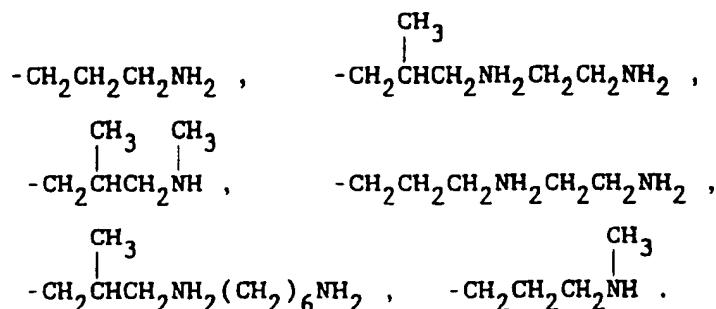
wherein each R^2 is independently selected from A and R^1 with the provision that at least one R^2 group be an amine functional group; and z has the value of 1 to 10. It is feasible to use amine functional compounds in which z has the value of greater than 10 to produce thioglycolamide functional siloxanes, however, the resulting thioglycolamide functional siloxanes produced from amine functional siloxanes in which z is greater than 10 are not useful in the perming of hair. when R^2 is not an amine functional group, it is preferred that R^2 be a methyl or phenyl group.

The amine functional group can be further exemplified by the formula

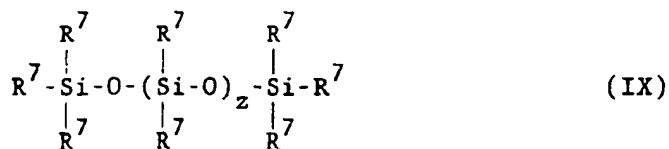
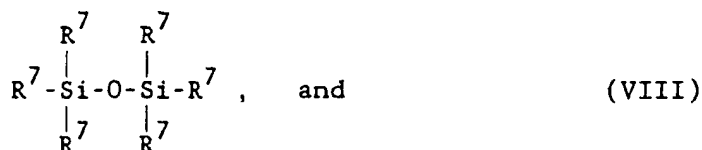


wherein each R^3 is independently selected from a straight or branched chain alkylene group consisting of 1 to 6 carbon atoms; R^4 is selected from the hydrogen atom, a straight or branched chain alkyl group consisting of 1 to 6 carbon atoms and the group $-\text{R}^3-\text{N}(\text{R}^5)-\text{H}$; and R^5 is selected from R^1 and the hydrogen atom. The amine-functional groups can comprise primary and secondary mono or diamines and mixtures thereof.

The amine functional group can be further exemplified by, but not limited to, the following structures



The amine-functional siloxanes used to produce thioglycolamide functional siloxanes useful in hair perming and conditioning can comprise mixtures of components varying in molecular weight and/or



and mixtures thereof;

wherein R^1 is as described above; A' is independently selected from R^1 and a thioglycolamide functional group with the provision that at least one A' group be a thioglycolamide functional group; R^7 is independently selected from A' and R^1 with the provision that at least one R^7 group be the thioglycolamide functional group; w has the value of 3 to 6; x has the value of 1 to 6; y has the value of 1 to 6; and z has the value of 1 to 10; with the provision that the sum of $x + y$ equals at least 3.

The thioglycolamide functional group can be further exemplified by the general formula



wherein R^3 is as described above; R^8 is selected from the hydrogen atom and the thioglycol functional group; R^9 is selected from the hydrogen atom, a straight or branched chain alkyl group consisting of 1 to 6 carbon atoms and the group $-\text{R}^3 - \text{N}(\text{R}^{10}) - \text{H}$; and R^{10} is selected from R^1 and R^8 ; with the provision that at least one of the R^8 and/or R^{10} groups is the thioglycol functional group.

The thioglycol functional group is represented by the general formula



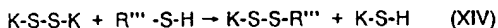
where R^6 is as described above.

Salts of the thioglycolamide functional siloxanes are formed as an intermediate in the process of forming the thioglycolamide functional siloxanes and may be isolated in a stable form. The salts of the siloxanes are the products formed prior to the removal of any water or subjecting the reaction mixture to heat other than that produced by the exotherm. The structure of the thioglycolamide salt may be further exemplified, for example, on a primary amine, by

It is preferred that the thioglycolamide siloxanes of the instant invention have a molecular weight of less than 1000 and more preferably of less than 500 for use on hair. The lower molecular weight materials are preferred so that they may diffuse into the hair, which is wound onto curling rods, in a relatively short period time. The resulting thioglycolamide siloxanes may contain a small amount of higher molecular weight materials (greater than 1000) introduced by impurities in the amine-functional siloxanes. These materials should only comprise a small amount of the total composition and the remainder should be comprised essentially of the lower molecular weight thioglycolamide materials.

The thioglycolamide siloxanes of this invention can be used in place of typical reducing agents in the curling of hair. The typical process for using the thioglycolamide siloxanes comprises washing and setting the hair by normal methods. The thioglycolamide siloxane is applied evenly on the hair. The treated hair is then allowed to stand at room temperature or in the presence of heat for a period sufficient to produce the desired curl. The hair is then water washed and treated with an oxidizing agent known in the art. The most typical oxidizing agent is an aqueous solution of hydrogen peroxide. After oxidation, the hair is then rinsed with water and styled in the desired manner.

It is theorized that the following reaction takes place on the hair when using the thioglycolamide functional siloxanes of this invention



where $R'''-S-H$ represents the thioglycolamide functional siloxane. Thus an amide-functional siloxane is incorporated into the hair structure during the process of reduction. It is further theorized that this incorporation of the siloxane into the hair is the means for imparting some conditioning effect to the hair. Thus, the thioglycolamide functional siloxanes of this invention are useful in the reduction of hair while simultaneously imparting some conditioning effects.

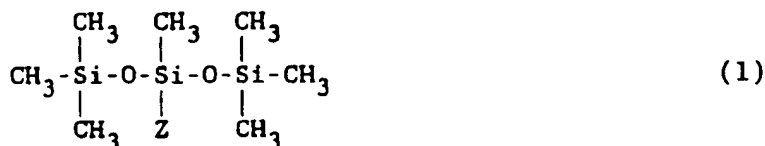
The thioglycolamide siloxanes of this invention, when used in the reduction of hair, are lower in odor than those that are currently commercially available for the reduction of hair. They produce a curl which is at least equal to that produced by typical reducing agents such as thioglycolic acid or thioglycolates. In addition, the thioglycolamide siloxanes of this invention impart improved settability of the treated hair as well as the above mentioned conditioning effects.

The salts of the thioglycolamide functional siloxanes are also useful in the perming and conditioning of hair.

So that those skilled in the art can understand and appreciate the invention taught herein, the following examples are presented, it being understood that these examples should not be used to limit the scope of this invention over the limitations found in the claims attached hereto.

EXAMPLE A

Preparation of



where Z is $-\text{CH}_2-\text{CH}(\text{CH}_3)-\text{CH}_2-\text{NH}-\text{CH}_2-\text{CH}_2-\text{NH}_2$.

A flask was equipped with a nitrogen source, thermometer, stirrer and a Dean-Stark trap and reflux condenser. The flask was purged with nitrogen and maintained under a nitrogen blanket during the entire operation. 309.5 grams of a mixture of $(\text{CH}_3-\text{Si}(\text{Z})-\text{O})_b$, where b equals 3 to 6, was placed in the flask with 400.5 grams of reagent grade xylene and 17.5 grams of potassium silanolate catalyst.

Heat was applied until a temperature of 141°C . was achieved. The reaction mixture was held at approximately 141°C . for a period of 1.5 hours during which time the xylene was refluxing. 2.7 grams of water and 18 grams of an unidentified hazy material were removed. The reaction product was stripped at 80° to 132°C . and 50 to 3 torr.

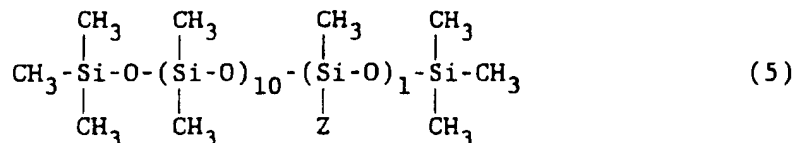
934.7 grams of hexamethyldisiloxane was added to the stripped reaction mixture. Heat was applied for 12 hours maintaining a temperature between 97.5° and 106.5°C . 1.8 grams of acetic acid and 10.4 grams

EXAMPLE E

Preparation of

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Using the same procedure as in Example D the material of formula 5 was produced. The reactants were 161.7 of the amine used in Example D, 288.1 grams of decamethyldisiloxane, 550.2 grams of a dimethyl cyclic siloxane mixture and 0.62 grams KOH. Following reaction at 135° C. for 5 hours, 1.02 grams of acetic acid and 10 grams additional cyclics were added. The product was stripped at 140° C. and 10 mm Hg for 2 hours. Amine Neutral Equivalents was measured to be 458.5.

EXAMPLE 1

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206.7 grams of the amine-functional siloxane produced in Example A was placed in a flask equipped with a nitrogen source, thermometer, stirrer and reflux condenser with a Dean-Stark trap. 51.3 grams of thioglycolic acid was added to the flask over a period of one hour while under a nitrogen blanket. A slight exotherm was observed. 128.3 grams of hexamethyldisiloxane was added and the mixture was heated to reflux for 4 hours. About 4.4 grams of water and 12.5 grams of hazy material was removed. The reaction product was two phases, a clear liquid top and white paste bottom. The top phase was decanted.

200.0 grams of absolute ethanol was added to the paste produced above. The mixture was heated to reflux and a clear homogeneous fluid formed in a few minutes.

EXAMPLE 2

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67.92 grams of the product produced in Example B as 112.8 grams of reagent grade toluene was placed in the flask used in Example 1. 37.4 grams of thioglycolic acid was added dropwise for a period of 105 minutes. A slight exotherm was observed. The reaction mixture was heated to reflux and held for 4.75 hours. Approximately 5.5 grams of water and 15.0 grams of a hazy material were removed. A two phase product resulted. The top phase was decanted. The bottom phase was a thick orange paste.

102.0 grams of ethanol was added to the paste produced above. The mixture was heated to a light reflux and held for 15 minutes. The product was a clear homogeneous fluid, golden colored.

EXAMPLE 3

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95.4 grams of the material produced in Example D and 122.3 grams of reagent grade toluene were placed in a flask. 46.0 of thioglycolic acid and 32.1 grams of toluene were mixed and added dropwise into the flask over a period of 10 minutes. A slight exotherm was observed. The mixture was heated to toluene reflux for 5 hours. A total of 6.9 grams of water was removed. The resulting mixture was two phases. The top phase was decanted. The bottom phase was an orange paste.

EXAMPLE 4

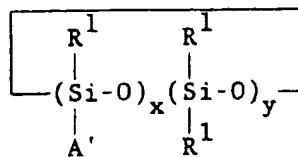
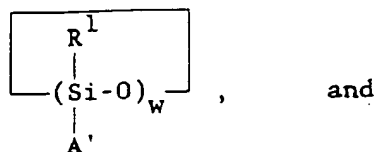
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Using the same procedure as in Example 3, the thioglycolamide was produced from the material in Example E. The reactants were 119.4 grams of the amine prepared in Example E, 61.2 grams of toluene (in pot), 23.93 grams TGA and an additional 41.2 grams toluene (with TGA). A two phase product resulted. The product was distilled at 38° to 40° C. and 30 torr. A red/orange opaque hazy fluid resulted.

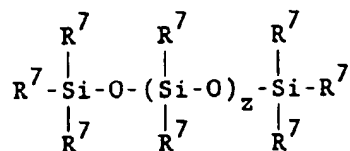
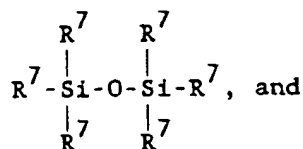
EXAMPLE 5

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81.29 grams of the material produced in Example C and 70.4 grams of xylene were placed in the flask. 49.7 grams of thioglycolic acid was added dropwise over a period of 20 minutes. An exotherm of 23° to



and linear siloxanes of the general formulas



and mixtures thereof;

wherein

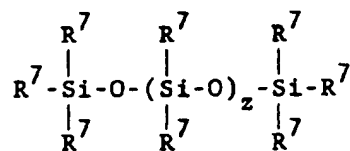
each R^1 is independently selected from an alkyl group containing 1 to 6 carbon atoms and an aryl group containing 6 to 10 carbon atoms;

each A' is independently selected from R^1 and a thioglycolamide functional group with the provision that at least one A' group be a thioglycolamide functional group;

each R^7 is independently selected from A' and R^1 with the provision that at least one R^2 group be a thioglycolamide functional group;

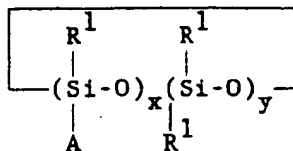
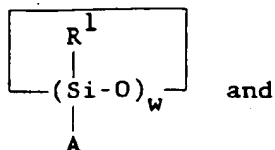
w has the value of 3 to 6; x has the value of 1 to 6; y has the value of 1 to 6; and z has the value of 1 to 10; with the provision that the sum of $x + y$ equals at least 3.

2. A composition as claimed in claim 1 wherein the thioglycolamide functional siloxane is of the formula

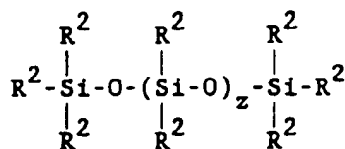
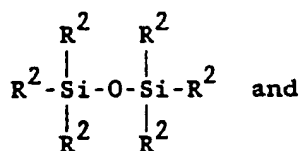


and R^7 is as described above.

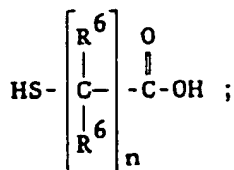
3. Salts of thioglycolamide functional siloxanes selected from the groups comprising cyclic siloxanes of the general formulas



and mixtures thereof; and
(ii) linear siloxanes of the general formulas



and mixtures thereof; with
(II) a thioglycolic acid of the general formula



B) subjecting the reaction mixture of (A) to heat to remove any water formed; and
C) recovering the reaction product of (B);

wherein

R¹ is independently selected from an alkyl group containing 1 to 6 carbon atoms and an aryl group containing 6 to 10 carbon atoms;

A is independently selected from R¹ and an amine functional group with the provision that at least one A group be an amine-functional group;

R² is independently selected from A and R¹ with the provision that at least one R² group be an amine functional group;

each R⁶ is independently selected from the hydrogen atom, R¹ and the group -NH₂;

w has the value of 3 to 6; x has the value of 1 to 6; y has the value of 1 to 6; z has the value of 1 to 10; and n has the value of 1 to 6; with the provision that the sum of x + y equals at least 3.

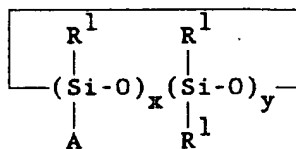
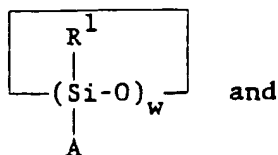
5. A process for preparing salts of thioglycolamide functional siloxanes comprising:

5. A process for preparing thioglycolamide functional siloxanes comprising:

A) reacting in the presence of heat

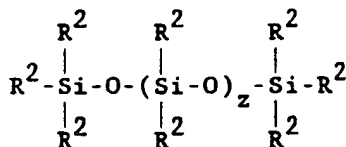
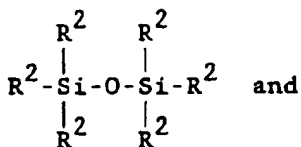
(I) amine-functional siloxanes selected from the groups comprising

(i) cyclic siloxanes of the general formulas



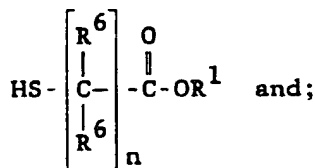
and mixtures thereof; and

(ii) linear siloxanes of the general formulas



and mixtures thereof; with

(II) an ester of thioglycolic acid of the general formula



(III) a catalyst

B) subjecting the reaction mixture of (A) to heat to remove any alcohol formed; and

C) recovering the reaction product of (B);

wherein

R¹ independently selected from an alkyl group containing 1 to 6 carbon atoms and an aryl group containing 6 to 10 carbon atoms;

A is independently selected from R¹ and an amine functional group with the provision that at least



DOCUMENTS CONSIDERED TO BE RELEVANT			EP 90314306.3
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
Y	<u>FR - A - 1 533 503</u> (DOW CORNING) * Totality * --	1, 2, 7	C 07 F 7/18 C 07 F 7/10 A 61 K 7/09 A 61 K 7/075
Y	<u>US - A - 4 832 948</u> (KONDO) * Claims; example * -----	1, 7	
			TECHNICAL FIELDS SEARCHED (Int. Cl.5)
			C 07 F A 61 K
The present search report has been drawn up for all claims			
Place of search VIENNA		Date of completion of the search 02-04-1991	Examiner MARCHART
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons Δ : member of the same patent family, corresponding document			

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